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**Aqueous coating material, process for its preparation,
 and its use**

The present invention relates to a novel aqueous
 5 coating material based on polyesters, polyurethane
 acrylates, amino resins, and pigments and/or fillers.
 The present invention also relates to a process for
 preparing the novel aqueous coating material. The
 present invention further relates to the use of the
 10 novel coating material as solid-color topcoat material
 or aqueous basecoat material for producing single-coat
 or multicoat color and/or effect paint systems,
 especially for bodies of commercial vehicles.

15 Aqueous coating materials based on polyacrylates,
 polyurethanes, polyesters, amino resins, and pigments
 and/or fillers are known from the European patents
 EP-B-0 521 919 or EP-B-0 593 454. On account of the
 mandatory presence therein of polyacrylates, these
 20 coating materials feature heightened solids content,
 fairly low tendency to run, and stabilization with
 respect to fluctuating shearing loads. The latter leads
 to improved settling characteristics, greater ease of
 handling, and increased reliability in application.

25

The polyurethanes that are used optionally therein are
 not polyurethane acrylates.

The optionally used polyesters are obtainable from at least one polyol and at least one polycarboxylic acid and/or at least one polycarboxylic anhydride. The polyols consist predominantly of aliphatic diols which
5 contain at least one alpha carbon atom which is secondary, tertiary, or a member of a carbon-containing ring system. The polycarboxylic acids and/or polycarboxylic anhydrides consist of aromatic and/or cycloaliphatic polycarboxylic acids and of
10 tricarboxylic and/or tetracarboxylic acids, which are used in such a way that they are incorporated into the polyesters on average by way of at least two carboxyl groups.

15 The known aqueous coating materials may be used as solid-color topcoat materials. Preferably, however, they are used as aqueous basecoat materials for finishing by the wet-on-wet process.

20 Aqueous coating materials based on polyurethane acrylates, polyesters, amino resins, and pigments and/or fillers are known from the European patent EP-B-0 730 613 and the German patent DE 197 05 219 A. Although it is stated that the polyurethane acrylates
25 are highly compatible with many binders used in addition, such as amino resins and polyester resins, for example, no further details are given regarding either the material composition of these additional binders or the amount in which they are to be employed.

These known coating materials, as well, may be used as solid-color topcoat materials. Preferably, however, they are used as aqueous basecoat materials for the wet-on-wet technique.

5

Whereas in the automobile segment the changeover from solid-color topcoats to two-coat finishes was completed years ago and the development of aqueous basecoat materials was carried on in parallel with this, no
10 changeover to two-coat finishes has yet been observed for the commercial vehicles. The reason for this is the expense that would necessarily be involved in relation to the application equipment. In order to provide commercial vehicle bodies with two-coat finishes, the
15 coating of the interiors would need to be fully automated, since during two-coat finishing the interiors would not be accessible, and so it would be necessary to install two separate application units and an additional predrying of the basecoat. Further, if
20 using conventional clearcoat materials or, with particular preference, two-component clearcoat materials in organic solution, account would have to be taken of the considerable level of emission of organic solvents.

25

The market is therefore calling for a solid-color topcoat material for painting commercial vehicles that provides solid-color topcoats whose optical quality and other properties at least correspond, if not indeed

exceed, those of the two-coat finishes. In view of environmental problems, moreover, the market is asking that such a solid-color topcoat material be aqueous while being able to be processed like a conventional topcoat material.

On account of the fact that the coating materials known to date and described at the outset were developed in particular for use as aqueous basecoat materials as part of two-coat painting by the wet-on-wet technique, they are unable when used as topcoat materials to meet the requirements to the extent that would be desirable.

The original solid-color topcoat material is required not least to be able to be used in addition as a refinish material on the line. For this purpose, crosslinking temperatures of 80 to 100°C are needed so as not to damage the completed commercial vehicles. With conventional solid-color topcoat materials based on alkyd resin/melamine resin, this is easy to ensure through the addition of strongly acidic catalysts. With the known aqueous coating materials described at the outset, however, which are dispersible in water by virtue of their binders being neutralized - with amines, in particular - such a solution, however, is naturally not an option.

But as to whether these known aqueous coating materials, with the addition of polyisocyanates,

provide aqueous two-component systems of durable stability and reliability in application which are suitable, particularly in the context of the finishing of commercial vehicles, for the solid-color topcoating
5 of plastics parts and as original refinish materials for solid-color topcoats, the patents cited at the outset are unforthcoming.

It is an object of the present invention to provide a
10 novel coating material which no longer has the disadvantages of the prior art but instead fully meets the market's requirements and is suitable in particular as a solid-color topcoat material for the OEM finishing of commercial vehicles and as an original refinish
15 material for line refinishing at comparatively low baking temperatures.

Found accordingly was the novel aqueous coating material which comprises

20

A) at least one water-soluble or -dispersible polyester,

B) at least one water-soluble or -dispersible
25 polyurethane acrylate,

C) at least one amino resin which per se or in the presence of ingredients (A) and (B) is water-soluble or -dispersible, and

D) at least one color and/or effect pigment and/or one filler, and also, if desired,

5 E) at least one polyisocyanate

and which is characterized in that the polyester (A) is preparable from

10 a1) a mixture comprising

a11) from 40 to 80 mol% of at least one aliphatic or cycloaliphatic polycarboxylic acid or at least one esterifiable derivative of an
15 aliphatic or cycloaliphatic polycarboxylic acid or a mixture of at least two of these starting products,

a12) from 20 to 60 mol% of at least one aromatic polycarboxylic acid, at least one
20 esterifiable derivative of an aromatic polycarboxylic acid or a mixture of at least two of these starting products;

25 and

a2) at least 60 mol% of at least one aliphatic or cycloaliphatic polyol whose molecule includes at least one structural element $-C(R^1R^2)-CH_2OH$ in

which the radicals R^1 and R^2 stand for aliphatic, cycloaliphatic or aromatic hydrocarbon radicals having from 1 to 20 carbon atoms or for methylol groups, or a mixture of at least two of these starting products.

In the text below, the novel aqueous coating material is referred to as "coating material of the invention" or, more specifically, as "solid-color topcoat material of the invention", "original refinish material of the invention" or "aqueous basecoat material of the invention".

Also found has been the novel process for preparing an aqueous coating material by mixing at least the following ingredients in an aqueous medium:

- A) at least one water-soluble or -dispersible polyester,
- B) at least one water-soluble or -dispersible polyurethane acrylate,
- C) at least one amino resin which per se or in the presence of ingredients (A) and (B) is water-soluble or -dispersible, and
- D) at least one color and/or effect pigment and/or one filler;

wherein the polyester (A) is preparable from

a1) a mixture comprising

5

a11) from 40 to 80 mol% of at least one aliphatic
or cycloaliphatic polycarboxylic acid or at
least one esterifiable derivative of an
aliphatic or cycloaliphatic polycarboxylic
10 acid or a mixture of at least two of these
starting products,

a12) from 20 to 60 mol% of at least one aromatic
polycarboxylic acid, at least one
15 esterifiable derivative of an aromatic
polycarboxylic acid or a mixture of at least
two of these starting products;

and

20

a2) at least 60 mol% of at least one aliphatic or
cycloaliphatic polyol whose molecule includes at
least one structural element $-C(R^1R^2)-CH_2OH$ in
which the radicals R^1 and R^2 stand for aliphatic,
25 cycloaliphatic or aromatic hydrocarbon radicals
having from 1 to 20 carbon atoms or for methylol
groups, or a mixture of at least two of these
starting products.

In the text below, the novel process for preparing a coating material is referred to as "first preparation process of the invention".

5 Also found has been a second novel process for preparing an aqueous coating material by

I) mixing at least the following ingredients in an aqueous medium:

10

A) at least one water-soluble or -dispersible polyester,

15

B) at least one water-soluble or -dispersible polyurethane acrylate,

C) at least one amino resin which per se or in the presence of ingredients (A) and (B) is water-soluble or -dispersible, and

20

D) at least one color and/or effect pigment and/or one filler;

to give component (I);

25

and

II) mixing component (I) with at least one polyisocyanate (E),

wherein the polyester (A) is preparable from

a1) a mixture comprising

5

a11) from 40 to 80 mol% of at least one aliphatic
or cycloaliphatic polycarboxylic acid or at
least one esterifiable derivative of an
aliphatic or cycloaliphatic polycarboxylic
10 acid or a mixture of at least two of these
starting products,

a12) from 20 to 60 mol% of at least one aromatic
polycarboxylic acid, at least one
15 esterifiable derivative of an aromatic
polycarboxylic acid or a mixture of at least
two of these starting products;

and

20

a2) at least 60 mol% of at least one aliphatic or
cycloaliphatic polyol whose molecule includes at
least one structural element $-C(R^1R^2)-CH_2OH$ in
which the radicals R^1 and R^2 stand for aliphatic,
25 cycloaliphatic or aromatic hydrocarbon radicals
having from 1 to 20 carbon atoms or for methylo
groups, or a mixture of at least two of these
starting products.

In the text below, the second novel process for preparing a coating material is referred to as "second preparation process of the invention".

5 In the light of the prior art it was surprising and unforeseeable for the skilled worker that the complex object on which the present invention is based could be achieved by means of the coating material of the invention. In particular it was surprising that the
10 solid-color topcoat material of the invention is outstandingly suitable for the low-emission coating of relatively large objects such as commercial vehicle bodies for which two-coat finishing by the wet-on-wet technique causes great problems, and that it provides
15 solid-color topcoats featuring good leveling, gloss, topcoat appearance, hardness, and practical solvent and chemical resistance. Even more surprising was that the coating material of the invention, especially the solid-color topcoat material of the invention, can be
20 used as a material base for the original refinish material of the invention.

The coating material of the invention may be a one-component (1K) system.

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In the context of the present invention, a one-component (1K) system is a thermosetting coating material wherein the binder and the crosslinking agent are present alongside one another, i.e., in one

component. A prerequisite for this is that the two ingredients crosslink with one another only at relatively high temperatures and, where appropriate, under exposure to actinic radiation.

5

The solid-color topcoat and aqueous basecoat material of the invention are preferably employed in this form.

The coating material of the invention may additionally
10 be a two-component or multicomponent system, but especially a two-component system.

In the context of the present invention this term refers to a coating material wherein in particular the
15 binder and the crosslinking agent are present separately from one another in at least two components which are not combined until shortly before application. This form is chosen when the binders and/or the solvents and/or dispersants react with the
20 crosslinking agents even at room temperature. Coating materials of this kind are employed in particular for coating heat-sensitive substrates, particularly in automotive refinish.

25 The original refinish material of the invention is preferably employed in this form. If the solid-color topcoat material of the invention is used to coat plastics parts, it is likewise used preferably in this form.

The first essential ingredient of the coating material of the invention is the polyester (A).

- 5 The polyester (A) is obtainable from the starting products (a1) and (a2).

The starting product (a1) for inventive use comprises a mixture of the starting products (a11) and (a12). In
10 accordance with the invention, the starting product (a11) is used in an amount of from 40 to 80 mol%, preferably from 50 to 70 mol%, and in particular from 55 to 65 mol%, and the starting product (a12) in an amount of from 20 to 60 mol%, preferably from 30 to
15 50 mol%, and in particular from 35 to 45 mol%.

The starting product (a11) is an aliphatic or cycloaliphatic polycarboxylic acid or an esterifiable derivative or a mixture of at least two of these
20 starting products.

Examples of suitable aliphatic polycarboxylic acids (a11) are linear or branched aliphatic polycarboxylic acids having from 2 to 80 carbon atoms in the molecule
25 and also their esterifiable derivatives, especially their anhydrides (where they exist), alkyl esters, aryl esters or halides, especially chlorides.

Examples of highly suitable aliphatic polycarboxylic

acids (all) are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, citric acid, 5 polymerized, especially dimerized, fatty acids, and their abovementioned esterifiable derivatives.

Polymerized, especially dimerized, fatty acids are obtainable by polymerizing fatty acids such as linoleic 10 acid, linolenic acid and/or oleic acid in a mixture, if desired, with saturated fatty acids. The result is a mixture which depending on reaction regime contains predominantly dimeric but also monomeric and trimeric molecules and also by-products. Normally, the reaction 15 mixture is purified by distillation. Commercial polymeric fatty acids (also called dimer fatty acids) contain at least 80% by weight, especially 98% by weight, of dimeric fatty acids, up to 20% by weight of trimeric fatty acids, and not more than 1% by weight of 20 monomeric fatty acids. They include both cyclic and linear aliphatic molecular fragments. In the context of the present invention, they are regarded, however, not as cycloaliphatic but rather as linear aliphatic polycarboxylic acids (all).

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Examples of suitable cycloaliphatic polycarboxylic acids (all) are 1,2-cyclobutanedicarboxylic acid, 1,3-cyclobutanedicarboxylic acid, 1,2-cyclopentanedicarboxylic acid, 1,3-cyclopentanedicarboxylic acid,

hexahydrophthalic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 4-methylhexahydrophthalic acid, tricyclodecanedicarboxylic acid, tetrahydrophthalic acid or 4-methyltetrahydrophthalic acid. They may be used both in their cis form and in their trans form, and also as a mixture of both forms.

The starting product (a12) is an aromatic polycarboxylic acids or an esterifiable derivative or a mixture of at least two of these starting products (a12).

Examples of highly suitable starting products (a12) are phthalic acid, isophthalic acid, terephthalic acid, pyromellitic acid, trimellitic acid, naphthalenedicarboxylic acids, naphthalenetetracarboxylic acids or naphthalenetetracarboxylic acids, halophthalic acids such as tetrachlorophthalic or tetrabromophthalic acid, and the esterifiable derivatives of these acids, particularly their anhydrides (where they exist), alkyl esters, aryl esters or halides, especially chlorides.

In accordance with the invention, use is made in particular of the dicarboxylic acids (a1) and/or their esterifiable derivatives. The tricarboxylic and/or tetracarboxylic acids (a1) and/or their esterifiable derivatives are used in order to introduce branching into the polyesters (A) for inventive use. In the context of the present invention they are used in such

amounts which do not lead to gelling of the polyesters
(A) for inventive use.

The starting product (a2) for inventive use comprises a
5 cycloaliphatic or aliphatic polyol or a mixture of at
least two of these starting products (a2).

Examples of suitable polyols (a2) are diols, triols and
tetrols, especially diols. Normally, triols and tetrols
10 are used alongside the diols in minor amounts in order
to introduce branching into the polyesters (A) for
inventive use. In the context of the present invention,
minor amounts are those amounts of triols and tetrols
which do not lead to gelling of the polyesters (A) for
15 inventive use.

The polyol (a2) molecule contains at least one
structural element $-C(R^1R^2)-CH_2OH$ in which the radicals
 R^1 and R^2 stand for aliphatic, cycloaliphatic or
20 aromatic hydrocarbon radicals having from 1 to 20
carbon atoms or for methylol groups.

In the context of the present inventions, aliphatic,
cycloaliphatic or aromatic hydrocarbon radicals are
25 substituted or unsubstituted alkyl, cycloalkyl, alkyl-
cycloalkyl, cycloalkylalkyl, aryl, alkylaryl, cyclo-
alkylaryl arylalkyl or arylcycloalkyl radicals.

Examples of suitable alkyl radicals are methyl, ethyl,

propyl, isopropyl, n-butyl, isobutyl, tert-butyl, amyl, hexyl, heptyl, octyl, 2-ethylhexyl, isooctyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl
5 or eicosanyl.

Examples of suitable cycloalkyl radicals are cyclobutyl, cyclopentyl, cyclohexyl, bicyclo[2.2.1]heptyl, bicyclo[3.2.1]octyl or tricyclodecyl.

10

Examples of suitable alkylcycloalkyl radicals are methylenecyclohexane, ethylenecyclohexane or propane-1,3-diyl-cyclohexane.

15 Examples of suitable cycloalkylalkyl radicals are 2-, 3-, or 4-methyl-, -ethyl-, -propyl- or -butylcyclohex-1-yl.

Examples of suitable aryl radicals are phenyl, naphthyl
20 or biphenylyl.

Examples of suitable alkylaryl radicals are benzyl-, ethylene- or propane-1,3-diylbenzene.

25 Examples of suitable cycloalkylaryl radicals are 2-, 3-, or 4-phenylcyclohex-1-yl.

Examples of suitable arylalkyl radicals are 2-, 3-, or 4-methyl-, -ethyl-, -propyl- or -butylphen-1-yl.

Examples of suitable arylcycloalkyl radicals are 2-, 3-, or 4-cyclohexylphen-1-yl.

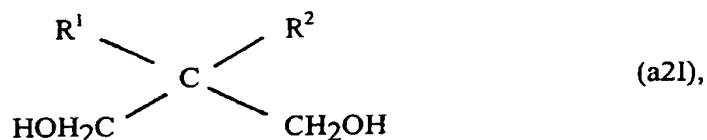
5 The radicals R^1 and/or R^2 described above may be substituted. For this purpose, electron withdrawing or electron donating atoms or organic radicals may be used.

10 Examples of suitable substituents are halogen atoms, especially chlorine and fluorine, partially or fully halogenated, especially chlorinated and/or fluorinated, alkyl, cycloalkyl, alkylcycloalkyl, cycloalkylalkyl, aryl, alkylaryl, cycloalkylaryl arylalkyl and aryl-
15 cycloalkyl radicals, including those exemplified above, especially tert-butyl; or aryloxy, alkyloxy and cycloalkyloxy radicals, especially phenoxy, naphthoxy, methoxy, ethoxy, propoxy, butyloxy or cyclohexyloxy.

20 Examples of especially suitable diols (a2) are neopentyl glycol hydroxypivalate, 2,2,4-trimethyl-1,5-pentanediol, 2,2,5-trimethyl-1,6-hexanediol, cyclohexane-1,1-dimethylol or cyclohexane-1,4-dimethyl-1,4-dimethylol.

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Further examples of especially suitable diols (a2) are the diols of the general formula a2I



in which the radicals R^1 and R^2 have the definition indicated above.

5

Examples of very particularly suitable diols (a2) of the general formula a2I are neopentyl glycol, 2-methyl-2-ethyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2-methyl-2-phenyl-1,3-propanediol, 2-methyl-2-cyclohexyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-butyl-2-methyl-1,3-propanediol, 2-phenyl-2-methyl-1,3-propanediol, 2-propyl-2-ethyl-1,3-propanediol, 2-di-tert-butyl-1,3-propanediol, 2-butyl-2-propyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, or 2,2-dipropyl-1,3-propanediol.

15

Examples of highly suitable triols (a2) are trimethylolethane and trimethylolpropane, especially trimethylolpropane.

20

Examples of highly suitable tetrols (a2) are pentaerythritol and homopentaerythritol.

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The polyester (A) for inventive use has a linear or branched chain. In accordance with the invention it is of advantage to use branched polyesters (A). Preferably, the degree of branching of the polyester

(A) is from 1.0 to 2.0, more preferably from 1.2 to 1.9, and in particular from 1.4 to 1.8, mol/kg.

The molecular weight of the polyester (A) for inventive
5 use may vary widely. It is, however, of advantage if it has a number-average molecular weight of from 650 to 2 500, preferably from 800 to 2 250, and in particular from 1 000 to 2 000 daltons.

10 Similarly, the acid number and the hydroxyl number of the polyester (A) for inventive use may vary widely. It is, however, of advantage if it has an acid number of from 25 to 55, preferably from 27 to 50, and in particular from 27 to 40, mg KOH/g. It is further of
15 advantage if the hydroxyl number is from 80 to 180, preferably from 100 to 170, and in particular from 120 to 160, mg KOH/g.

Preparation of the polyester (A) for inventive use has
20 no special features in terms of its method but instead takes place in accordance with the customary and known methods of polyester chemistry by the reaction of the starting products (a1) and (a2). In accordance with the invention it is of advantage in this context if the
25 starting products (a1) and (a2) are reacted with one another in a molar ratio $(a1):(a2) = (1.1-2):1$, preferably $(1.2-1.7):1$, and in particular $(1.25-1.6):1$. The reaction temperatures are preferably from 140 to 240°C and in particular from 180 to 220°C. For removing

water of reaction it is advantageous to use an azeotrope former such as cyclohexane. In some cases it is appropriate to catalyze the esterification reaction. Examples of suitable catalysts are heterogeneous catalysts such as transition metal oxides and rare earth oxides or homogeneous catalysts such as tetrabutyl titanate, zinc octoate or dibutyltin oxide.

In the course of their preparation or in the course of their dispersion in an aqueous medium the polyesters (A) for inventive use are neutralized. Examples of suitable neutralizing agents are the compounds described below and suitable for neutralizing the functional groups (b32) convertible into anions. Of these, it is preferred to use the readily volatile amines and also the alkanol amines, but especially the alkanol amines.

The second essential ingredient of the coating material of the invention is at least one water-soluble or -dispersible polyurethane acrylate (B). This is at least one polyurethane which is grafted with olefinically unsaturated monomers, ionically stabilized and/or nonionically stabilized and which contains lateral and/or terminal olefinically unsaturated groups. It is obtainable by carrying out free-radical polymerization in an aqueous dispersion in the presence

B1) of at least one dispersed polyurethane resin

obtainable from

b1) at least one polyisocyanate alone or together
with at least one monoisocyanate;

5

b2) at least one polyester polyol and/or
polyether polyol having a number-average
molecular weight of from 400 to 5 000;

10

b3) at least one compound containing

b31) at least one isocyanate-reactive group
and also

15

b32) at least one group which is anionic
and/or is convertible into anions by
neutralizing agents and/or

b33) at least one nonionic hydrophilic group;

20

and also

b4) at least one compound containing

25

b41) at least one isocyanate-reactive group
and

b42) at least one olefinically unsaturated
group;

B2) of at least one olefinically unsaturated monomer,

the weight ratio of polyurethane resin (B1) to
5 olefinically unsaturated monomer (B2) being preferably
from 1:10 to 10:1.

Depending on the manner of its stabilization, the
polyurethane (B1) advantageously has an acid number or
10 amine number of from 10 to 250 mg KOH/g (ionic
stabilization or nonionic plus ionic stabilization) or
from 0 to 10 mg KOH/g (nonionic stabilization), an OH
number of from 30 to 350 mg KOH/g, and a number-average
molecular weight of from 1 500 and 55 000 daltons. The
15 olefinically unsaturated double bond content is
advantageously on average from 0.2 to 3, preferably
from 0.4 to 2, and in particular from 0.5 to 1.5, per
molecule.

20 Examples of suitable polyisocyanates (b1) are diiso-
cyanates (b1) and triisocyanates (b1). It is
advantageous to use diisocyanates (b1). The triiso-
cyanates (b1) are used in minor amounts in order to
introduce branching into the molecule chains. In the
25 context of the present invention, minor amounts are
those amounts which do not induce gelling of the
polyurethane (B1). In some cases it is found
advantageous to use chain-terminating monoisocyanates
(b1).

Examples of highly suitable diisocyanates (b1) are isophorone diisocyanate (= 5-isocyanato-1-isocyanato-methyl-1,3,3-trimethylcyclohexane), 5-isocyanato-1-(2-isocyanatoeth-1-yl)-1,3,3-trimethylcyclohexane, 5-isocyanato-1-(3-isocyanatoprop-1-yl)-1,3,3-trimethylcyclohexane, 5-isocyanato-(4-isocyanatobut-1-yl)-1,3,3-trimethylcyclohexane, 1-isocyanato-2-(3-isocyanatoprop-1-yl)cyclohexane, 1-isocyanato-2-(3-isocyanatoeth-1-yl)cyclohexane, 1-isocyanato-2-(4-isocyanatobut-1-yl)cyclohexane, 1,2-diisocyanatocyclobutane, 1,3-diisocyanatocyclobutane, 1,2-diisocyanatocyclopentane, 1,3-diisocyanatocyclopentane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatocyclohexane, dicyclohexylmethane 2,4'-diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, ethylethylene diisocyanate, trimethylhexane diisocyanate, heptanemethylene diisocyanate or diisocyanates derived from dimer fatty acids, such as are sold under the commercial designation DDI 1410 by the company Henkel and described in the patents WO 97/49745 and WO 97/49747, especially 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane, or 1,2-, 1,4- or 1,3-bis(isocyanatomethyl)cyclohexane, 1,2-, 1,4- or 1,3-bis(2-isocyanatoeth-1-yl)cyclohexane, 1,3-bis(3-isocyanatoprop-1-yl)cyclohexane, 1,2-, 1,4- or 1,3-bis(4-isocyanatobut-1-yl)cyclohexane, liquid bis(4-isocyanatocyclohexyl)methane with a trans/trans

content of up to 30% by weight, preferably 25% by weight, and in particular 20% by weight, such as is described by the patents DE-A-44 14 032, GB-A-1220717, DE-A-16 18 795 or DE-A-17 93 785; tolylene diisocyanate, xylylene diisocyanate, bisphenylene diisocyanate, naphthylene diisocyanate or diphenylmethane diisocyanate.

Examples of highly suitable triisocyanates (b1) are the isocyanurates of the above-described diisocyanates (b1).

Examples of highly suitable monoisocyanates (b1) are phenyl isocyanate, cyclohexyl isocyanate or stearyl isocyanate.

The polyester polyols (b2) have a number-average molecular weight of from 400 to 5 000.

Examples of suitable polyester polyols (b2) are saturated or olefinically unsaturated polyester polyols (b2) which are prepared by reacting

- unsulfonated or sulfonated saturated and/or unsaturated polycarboxylic acids or their esterifiable derivatives, together if desired with monocarboxylic acids, and also

- saturated and/or unsaturated polyols, together if

desired with monools.

Examples of suitable polycarboxylic acids are aromatic, aliphatic and cycloaliphatic polycarboxylic acids.

- 5 Preference is given to using aromatic and/or aliphatic polycarboxylic acids.

Examples of highly suitable aliphatic and cycloaliphatic polycarboxylic acids are the above-described
10 starting products (a11).

Examples of highly suitable aromatic polycarboxylic acids are the above-described starting products (a12).

- 15 If desired, together with the polycarboxylic acids it is also possible to use monocarboxylic acids, such as benzoic acid, tert-butylbenzoic acid, lauric acid, isononanoic acid, fatty acids of naturally occurring oils, acrylic acid, methacrylic acid, ethacrylic acid
20 or crotonic acid, for example. Isononanoic acid is a preferred monocarboxylic acid used.

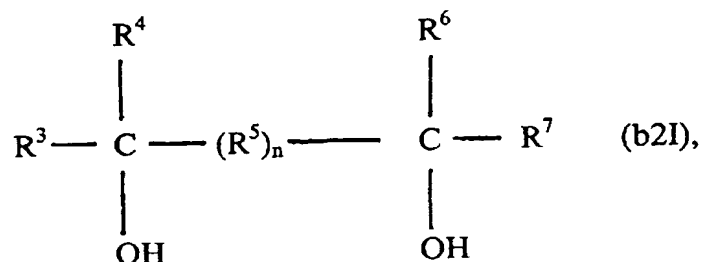
Examples of highly suitable polyols are the above-described diols, triols and tetrols (a2), especially
25 the diols. Normally, triols and/or tetrols are used alongside the diols in minor amounts in order to introduce branching into the polyester polyols (b2).

Further examples of highly suitable diols are ethylene

glycol, 1,2- or 1,3-propanediol, 1,2-, 1,3- or 1,4-
butanediol, 1,2-, 1,3-, 1,4- or 1,5-pentanediol, 1,2-,
1,3-, 1,4-, 1,5- or 1,6-hexanediol, diethylene glycol,
1,2-, 1,3- or 1,4-cyclohexanediol, 1,2-, 1,3- or
5 1,4-cyclohexanedimethanol or the positionally isomeric
diethyloctanediols.

Further examples of highly suitable diols are diols of
the formula b2I:

10



in which R^3 , R^4 , R^6 and R^7 each represent identical
or different radicals and stand for an alkyl
15 radical having from 1 to 6 carbon atoms, a cyclo-
alkyl radical or an aryl radical and R^5 represents
an alkyl radical having from 1 to 6 carbon atoms,
an aryl radical or an unsaturated alkyl radical
having from 1 to 6 carbon atoms, and n is either 0
20 or 1.

Examples of suitable alkyl radicals, cycloalkyl
radicals or aryl radicals are described above.

25 Examples of suitable unsaturated alkyl radicals are the

above-described alkyl radicals which contain at least one olefinically unsaturated double bond in the chain.

As diols II of the general formula II it is possible,
5 for example, to use 2,5-dimethyl-2,5-hexanediol,
2,5-diethyl-2,5-hexanediol, 2-ethyl-5-methyl-2,5-hexanediol, 2,4-dimethyl-2,4-pentanediol, 2,3-dimethyl-2,3-butanediol, 1,4-(2'-hydroxypropyl)benzene and 1,3-(2'-hydroxypropyl)benzene.

10

Of all these diols, 1,6-hexanediol and neopentyl glycol are particularly advantageous and are therefore used with particular preference.

15 These diols may also be used per se alongside the polyester polyols and/or polyether polyols (b2) for preparing the polyurethanes (B1).

A further example of a suitable triol is glycerol.

20

The triols may also be used per se alongside the polyester polyols and/or polyether polyols (b2) for preparing the polyurethanes (B1) (cf. the patent EP-A-0 339 433).

25

If desired, minor amounts of chain-terminating monools may be used as well. Examples of suitable monools are alcohols or phenols such as ethanol, propanol, n-butanol, sec-butanol, tert-butanol, amyl alcohols,

hexanols, fatty alcohols, allyl alcohol or phenol.

The polyester polyols (b2) may be prepared as described above for the polyesters (A).

5

Further examples of suitable polyester polyols (b2) are polyester diols (b2) which are obtained by reacting a lactone with a diol. They are notable for the presence of terminal hydroxyl groups and recurring polyester
10 fractions of the formula $-(\text{CO}-(\text{CHR}^8)_m-\text{CH}_2-\text{O})-$. Here, the index m is preferably from 4 to 6 and the substituent R^8 = hydrogen, an alkyl radical, cycloalkyl radical or alkoxy radical. No one substituent contains more than 12 carbon atoms. The overall number of carbon
15 atoms in the substituent does not exceed 12 per lactone ring. Examples thereof are hydroxycaproic acid, hydroxybutyric acid, hydroxydecanoic acid and/or hydroxystearic acid.

20 For the preparation of the polyester diols, preference is given to the unsubstituted ###-caprolactone, in which m has the value 4 and all R^8 substituents are hydrogen.

25 The reaction with lactone is started by low molecular mass polyols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol or dimethylolcyclohexane. It is, however, also possible to react other reaction components, such as ethylenediamine, alkyldialkanol-

amines or else urea, with caprolactone. Further suitable diols of relatively high molecular mass include polylactam diols, which are prepared by reacting, for example, ###-caprolactam with low
5 molecular mass diols.

Examples of suitable polyether polyols (b2) are polyether diols (b2) of the general formula $H-(-O-(CHR^9)_o-)_pOH$, where the substituent R^9 = hydrogen
10 or a lower, unsubstituted or substituted alkyl radical, the index $o = 2$ to 6 , preferably 3 to 4 , and the index $p = 2$ to 100 , preferably 5 to 50 . As especially suitable examples, mention is made of linear or branched polyether diols such as poly(oxyethylene)
15 glycols, poly(oxypropylene) glycols and poly(oxybutylene) glycols.

The polyether diols should on the one hand not introduce excessive amounts of ether groups, since
20 otherwise the polyurethane acrylates (B) for inventive use that are formed start to swell in water. On the other hand, they may be used in amounts which ensures the nonionic stabilization of the polyurethane acrylates (B). In that case they serve as the
25 functional nonionic groups (b34) described below.

The polyurethane (B1) contains

(b32) functional groups which can be converted into

anions by neutralizing agents, and/or anionic groups

and/or

5

(b34) nonionic hydrophilic groups.

Examples of suitable functional groups (b32) which can be converted into anions by neutralizing agents are
10 carboxylic acid, sulfonic acid or phosphonic acid groups, especially carboxylic acid groups.

Examples of suitable anionic groups (b32) for inventive use are carboxylate, sulfonate or phosphonate groups,
15 especially carboxylate groups.

Examples of suitable neutralizing agents for functional groups (b32) transformable into anions are ammonia, ammonium salts, such as ammonium carbonate or ammonium
20 hydrogen carbonate, for example, and also amines, such as, e.g., trimethylamine, triethylamine, tributylamine, N-methyl-, N-ethyl-, N-propyl- or N-butylmorpholine, dimethylaniline, diethylaniline, triphenylamine, dimethylethanolamine, diethylethanolamine, methyl-
25 diethanolamine, triethanolamine and the like. The neutralization may take place in organic phase or in aqueous phase. A preferred neutralizing agent used is dimethylethanolamine.

The amount of neutralizing agent used is chosen so that from 1 to 100 equivalents, preferably from 50 to 90 equivalents, of the functional groups (b32) or (b33) of the polyurethane (B1) or of the polyurethane acrylate (B) are neutralized.

The introduction of (potentially) anionic groups (b32) into the polyurethane molecules takes place by the incorporation of compounds (b3) containing per molecule at least one isocyanate-reactive group (b31); the amount to be used may be calculated from the target acid number.

Examples of highly suitable compounds (b3) are those containing per molecule two isocyanate-reactive groups (b31). Particularly suitable isocyanate-reactive groups (b31) are hydroxyl groups, and also primary and/or secondary amino groups. Accordingly, it is possible, for example, to use alkanolic acids having two substituents on the α carbon atom. The substituent may be a hydroxyl group, an alkyl group or, preferably, an alkylol group. These alkanolic acids have at least one, generally from 1 to 3, carboxyl groups in the molecule. They have from 2 to about 25, preferably from 3 to 10, carbon atoms. Examples of suitable alkanolic acids are dihydroxypropionic acids, dihydroxysuccinic acid, and dihydroxybenzoic acid. One particularly preferred group of alkanolic acids are the α,α -dimethylolalkanoic acids of the general formula

$R^{10}-C(CH_2OH)_2COOH$, where R^{10} stands for a hydrogen atom or an alkyl group having up to about 20 carbon atoms. Examples of especially suitable alkanolic acids are 2,2-dimethylolacetic acid, 2,2-dimethylolpropionic acid, 2,2-dimethylolbutyric acid, and 2,2-dimethylolpentanoic acid. The preferred dihydroxyalkanoic acid is 2,2-dimethylolpropionic acid. Examples of compounds containing amino groups are ###,###-diaminovaleric acid, 3,4-diaminobenzoic acid, 2,4-diaminotoluene-sulfonic acid, and 2,4-diaminodiphenyl ether sulfonic acid.

Nonionic stabilizing poly(oxyalkylene) groups (b33) may be introduced as lateral or terminal groups into the polyurethane molecules. For this purpose it is possible, for example, to use alkoxypoly(oxyalkylene) alcohols having the general formula $R^{11}O-(-CH_2-CH^{12}-O-)_rH$ in which R^{11} stands for an alkyl radical having from 1 to 6 carbon atoms, R^{12} for a hydrogen atom or an alkyl radical having 1 to 6 carbon atoms, and the index r for a number between 20 and 75. (cf. the patents EP-A-0 354 261 or EP-A-0 424 705).

The polyurethane (B1) contains olefinically unsaturated groups (b42). Advantageously they are introduced with the aid of at least one compound (b4) which contains at least one isocyanate-reactive group (b41) and at least one olefinically unsaturated group (b42). Examples of suitable groups (b41) are the abovementioned groups

(b31). Examples of suitable groups (b42) are acrylic, vinylic or allylic double bonds. Examples of suitable compounds (b4) are hydroxy (meth)acrylates, especially hydroxyalkyl (meth)acrylates such as hydroxyethyl, 5 hydroxypropyl, or hydroxyhexyl (meth)acrylate or 2,3-dihydroxypropyl (meth)acrylate, 2,3-dihydroxypropyl monoallyl ether, allyl 2,3-dihydroxypropanoate, glycerol mono(meth)acrylate, glycerol monoallyl ether, pentaerythritol mono(meth)acrylate, pentaerythritol 10 di(meth)acrylate, pentaerythritol monoallyl ether, pentaerythritol diallyl ether, trimethylolpropane monoallyl ether, trimethylolpropane mono(meth)acrylate, and trimethylolpropane diallyl ether. Examples of highly suitable compounds (b4) are trimethylolpropane 15 monoallyl ether, glycerol mono(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol diallyl ether, glycerol monoallyl ether, and trimethylolpropane mono(meth)acrylate, but especially trimethylolpropane monoallyl ether, glycerol monoallyl ether, and allyl 20 2,3-dihydroxypropanoate. The compounds (b4) containing at least two groups (b41) are preferably incorporated into the chain of the polyurethane molecules (B1).

The polyurethane (B1) may be chain extended before or 25 after its reaction with the olefinically unsaturated monomers (B2). Examples of suitable chain extenders are polyols, polyamines, and amino alcohols.

Suitable polyols for the chain extension are polyols

having up to 36 carbon atoms per molecule such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,2-butylene glycol, 1,6-hexanediol, trimethylolpropane, castor oil or hydrogenated castor oil, di-
5 trimethylolpropane ether, pentaerythritol, 1,2-cyclohexanediol, 1,4-cyclohexanedimethanol, bisphenol A, bisphenol F, neopentyl glycol, neopentyl glycol hydroxypivalate, hydroxyethylated or hydroxypropylated
10 bisphenol A, hydrogenated bisphenol A, or mixtures thereof (cf. patents EP-A-0 339 433, EP-A-0 436 941, EP-A-0 517 707).

Examples of suitable polyamines contain at least two
15 primary and/or secondary amino groups. Polyamines are essentially alkylene polyamines having from 1 to 40 carbon atoms, preferably from about 2 to 15 carbon atoms. They may carry substituents which have no hydrogen atoms that are reactive with isocyanate
20 groups. Examples are polyamines having a linear or branched aliphatic, cycloaliphatic or aromatic structure and containing at least two primary amino groups.

25 Diamines that may be mentioned include hydrazine, ethylenediamine, propylenediamine, 1,4-butylenediamine, piperazine, 1,4-cyclohexyldimethylamine, hexamethylene-1,6-diamine, trimethylhexamethylenediamine, methane-diamine, isophoronediamine, 4,4'-diaminodicyclo-

hexylmethane, and aminoethyleneethanolamine. Preferred diamines are hydrazine, alkyl- or cycloalkyldiamines such as propylenediamine and 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane.

5

It is also possible to use polyamines, which contain more than two amino groups in the molecule. In such cases, however, it is necessary to ensure - by using monoamines as well, for example - that no crosslinked
10 polyurethane resins are obtained. Polyamines of this kind which can be used are diethylenetriamine, triethylenetetramine, dipropylenetriamine, and dibutyl-
enetriamine. An example of a monoamine that may be mentioned is ethylhexylamine (cf. the patent
15 EP-A-0 089 497).

Examples of suitable amino alcohols are ethanolamine or diethanolamine.

20 The polyurethanes (B1) are reacted with at least one olefinically unsaturated monomer (B2) to give the polyurethane acrylates (B) for inventive use. In this case it is preferred to employ the conditions of free-radical addition polymerization in emulsion or
25 dispersion.

Examples of suitable monomers (B2) are

B21) substantially acid group-free (meth)acrylic

esters such as (meth)acrylic alkyl or cycloalkyl esters having up to 20 carbon atoms in the alkyl radical, especially methyl, ethyl, propyl, n-butyl, sec-butyl, tert-butyl, hexyl, ethylhexyl, stearyl and lauryl acrylate or methacrylate; cycloaliphatic (meth)acrylic esters, especially cyclohexyl, isobornyl, dicyclopentadienyl, octahydro-4,7-methano-1H-indenemethanol acrylate or tert-butylcyclohexyl (meth)acrylate; (meth)acrylic oxaalkyl esters or oxacycloalkyl esters such as ethyltriglycol (meth)acrylate and methoxyoligoglycol (meth)acrylate having a molecular weight Mn of preferably 550, or other ethoxylated and/or propoxylated hydroxyl-free (meth)acrylic acid derivatives. These may contain minor amounts of (meth)acrylic alkyl or cycloalkyl esters of higher functionality, such as the di(meth)acrylates of ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, butylene glycol, 1,5-pentanediol, 1,6-hexanediol, octahydro-4,7-methano-1H-indene-dimethanol or 1,2-, 1,3- or 1,4-cyclohexanediol; trimethylolpropane di- or tri(meth)acrylate; or pentaerythritol di-, tri- or tetra(meth)acrylate. For the purposes of the present invention, minor amounts of monomers of higher functionality in this case are to be understood as amounts which do not lead to crosslinking or gelling of the copolymers (A).

B22) Monomers which carry per molecule at least one hydroxyl group, amino group, alkoxymethylamino group or imino group and are essentially free from acid groups, such as hydroxyalkyl esters of acrylic acid, methacrylic acid or another alpha,beta-olefinically unsaturated carboxylic acid, which derive from an alkylene glycol esterified with the acid, or which are obtainable by reacting the alpha,beta-olefinically unsaturated carboxylic acid with an alkylene oxide, especially hydroxyalkyl esters of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid in which the hydroxyalkyl group contains up to 20 carbon atoms, such as 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-hydroxybutyl, 4-hydroxybutyl acrylate, methacrylate, ethacrylate, crotonate, maleate, fumarate or itaconate; or hydroxycycloalkyl esters such as 1,4-bis(hydroxymethyl)cyclohexane, octahydro-4,7-methano-1H-indenedimethanol or methylpropanediol monoacrylate, monomethacrylate, monoethacrylate, monocrotonate, monomaleate, monofumarate or monoitaconate; or reaction products of cyclic esters, such as epsilon-caprolactone, for example, and these hydroxyalkyl or hydroxycycloalkyl esters; or olefinically unsaturated alcohols such as allyl alcohol or

polyols such as trimethylolpropane monoallyl or diallyl ether or pentaerythritol monoallyl, diallyl or triallyl ether (as far as these monomers (a2) of higher functionality are concerned, the comments made above relating to the monomers (a1) of higher functionality apply similarly); N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl methacrylate, allylamine or N-methylaminoethyl acrylate or N,N-di(methoxymethyl)aminoethyl acrylate and methacrylate or N,N-di(butoxymethyl)aminopropyl acrylate and methacrylate; monomers of this kind are used preferably to prepare self-crosslinking ingredients (A).

15

B23) Monomers which carry per molecule at least one acid group which can be converted into the corresponding acid anion group, such as acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid; olefinically unsaturated sulfonic or phosphonic acids or their partial esters; or mono(meth)acryloyloxyethyl maleate, succinate or phthalate.

20

25 B24) Vinyl esters of alpha-branched monocarboxylic acids having 5 to 18 carbon atoms in the molecule. The branched monocarboxylic acids can be obtained by reacting formic acid or carbon monoxide and water with olefins in the presence

of a liquid, strongly acidic catalyst; the olefins may be cracking products of paraffinic hydrocarbons, such as mineral oil fractions, and may comprise both branched and straight-chain acyclic and/or cycloaliphatic olefins. Reacting such olefins with formic acid or, respectively, with carbon monoxide and water produces a mixture of carboxylic acids in which the carboxyl groups are located predominantly on a quaternary carbon atom. Examples of other olefinic starting materials are propylene trimer, propylene tetramer and diisobutylene. Alternatively, the vinyl esters (a4) may be prepared in a conventional manner from the acids, by reacting, for example, the acid with acetylene. Particular preference, owing to their ready availability, is given to using vinyl esters of saturated aliphatic monocarboxylic acids having 9 to 11 carbon atoms that are branched on the alpha carbon atom, but especially Versatic® acids.

B25) Reaction products of acrylic acid and/or methacrylic acid with the glycidyl ester of an alpha-branched monocarboxylic acid having 5 to 18 carbon atoms per molecule, especially a Versatic® acid, or, instead of the reaction product, an equivalent amount of acrylic acid and/or methacrylic acid which is then reacted during or after the polymerization reaction with the

glycidyl ester of an alpha-branched monocarboxylic acid having 5 to 18 carbon atoms per molecule, especially a Versatic® acid.

- 5 B26) Cyclic and/or acyclic olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, cyclohexene, cyclopentene, norbornene, butadiene, isoprene, cyclopentadiene and/or dicyclopentadiene.
- 10
- B27) (Meth)acrylamides such as (meth)acrylamide, N-methyl-, N,N-dimethyl-, N-ethyl-, N,N-diethyl-, N-propyl-, N,N-dipropyl-, N-butyl-, N,N-dibutyl-, N-cyclohexyl-, N,N-cyclohexylmethyl- and/or
- 15 N-methylol-, N,N-dimethylol-, N-methoxymethyl-, N,N-di(methoxymethyl)-, N-ethoxymethyl- and/or N,N-di(ethoxyethyl)-(meth)acrylamide.
- B28) Monomers containing epoxide groups, such as the
- 20 glycidyl ester of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid and/or itaconic acid.
- B29) Vinylaromatic hydrocarbons such as styrene,
- 25 alpha-alkylstyrenes, especially alpha-methylstyrene, and/or vinyltoluene; vinylbenzoic acid (all isomers), N,N-diethylaminostyrene (all isomers), alpha-methylvinylbenzoic acid (all isomers), N,N-diethylamino-alpha-methylstyrene

(all isomers) and/or p-vinylbenzenesulfonic acid.

B210) Nitriles such as acrylonitrile and/or methacrylonitrile.

5

B211) Vinyl compounds, especially vinyl halides and/or vinylidene dihalides such as vinyl chloride, vinyl fluoride, vinylidene dichloride or vinylidene difluoride; N-vinylamides such as vinyl-N-methylformamide, N-vinylcaprolactam, 1-vinylimidazole or N-vinylpyrrolidone; vinyl ethers such as ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether and/or vinyl cyclohexyl ether; and/or vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate and/or the vinyl ester of 2-methyl-2-ethylheptanoic acid.

20 B212) Allyl compounds, especially allyl ethers and allyl esters such as allyl methyl, ethyl, propyl or butyl ether or allyl acetate, propionate or butyrate.

25 B213) Polysiloxane macromonomers having a number-average molecular weight M_n of from 1000 to 40 000 and having on average from 0.5 to 2.5 ethylenically unsaturated double bonds per molecule; especially polysiloxane macromonomers

having a number-average molecular weight M_n of
from 2000 to 20 000, with particular preference
from 2500 to 10 000 and, in particular, from 3000
to 7000 and having on average from 0.5 to 2.5,
5 preferably from 0.5 to 1.5, ethylenically
unsaturated double bonds per molecule, as are
described in DE-A-38 07 571 on pages 5 to 7, in
DE-A-37 06 095 in columns 3 to 7, in
EP-B-0 358 153 on pages 3 to 6, in US-A 4,754,014
10 in columns 5 to 9, in DE-A-44 21 823 or in the
international patent application WO 92/22615 on
page 12 line 18 to page 18 line 10.

and/or

15

B214) Acryloxysilane-containing vinyl monomers,
preparable by reacting hydroxyl-functional
silanes with epichlorohydrin and then reacting
the reaction product with (meth)acrylic acid
20 and/or with hydroxyalkyl and/or hydroxycycloalkyl
esters of (meth)acrylic acid (cf. monomers B2).

Further examples of suitable monomers (B2) are known
from the European patent EP-B-0 730 613.

25

Preference is given to employing mixtures of the
monomers (B21), (B22), and (B23). The composition of
the mixtures may vary very widely. In general it is
advisable to choose the following composition:

(B21): from 50 to 95% by weight, preferably from 55 to 90% by weight, and in particular from 60 to 85% by weight;

5

(B22): from 2 to 30% by weight, preferably from 3 to 25% by weight, and in particular from 4 to 20% by weight and

10 (B23): from 2 to 25% by weight, preferably from 3 to 20% by weight, and in particular from 4 to 15% by weight.

The percentages by weight here are based in each case
15 on the overall amount of the mixture of monomers (B2).

The monomers (B2) are reacted in the presence of at least one free-radical initiator. Examples of initiators which can be used include the following:
20 dialkyl peroxides, such as di-tert-butyl peroxide or dicumyl peroxide; hydroperoxides, such as cumene hydroperoxide or tert-butyl hydroperoxide; per esters, such as tert-butyl perbenzoate, tert-butyl perpivalate, tert-butyl per-3,5,5-trimethylhexanoate or tert-butyl
25 per-2-ethylhexanoate; potassium peroxodisulfate, sodium peroxodisulfate or ammonium peroxodisulfate; azo dinitriles such as azobisisobutyronitrile; C-C-cleaving initiators such as benzpinacol silyl ethers; or a combination of a nonoxidizing initiator with hydrogen

peroxide.

In accordance with the invention, the graft copolymerization is conducted in an aqueous medium.

5

The aqueous medium contains substantially water. In this context, the aqueous medium may contain minor amounts of the below-detailed crosslinking agents (C) and also the below-detailed further ingredients (F) to
10 (M) and/or other dissolved solid, liquid or gaseous organic and/or inorganic, low and/or high molecular mass substances, especially surface-active substances, provided they do not adversely affect, let alone inhibit, the graft copolymerization. In the context of
15 the present invention, the term "minor amount" is to be understood as an amount which does not take away the aqueous character of the aqueous medium.

The aqueous medium may also, however, be straight
20 water.

The graft copolymerization is advantageously conducted at temperatures above room temperature and below the lowest decomposition temperature of the monomers (B2)
25 that are used in each case, it being preferred to choose a temperature range from 10 to 150°C, with very particular preference from 70 to 120°C, and in particular from 80 to 110°C.

When using particularly volatile monomers (B2) the graft copolymerization may also be conducted under pressure, preferably under from 1.5 to 3 000 bar, more preferably from 5 to 1 500, and in particular from 10 to 1 000 bar.

The nature and amount of the monomers (B2) are selected so as to give the polyurethane acrylates (B) for inventive use with the specification described above.

10 Therefore, depending on the monomers (B2) employed, the skilled worker will easily be able to determine the appropriate amount on the basis of his or her art knowledge, with the assistance where appropriate of simple preliminary tests. The polyurethanes (B1) and

15 the monomers (B2) are preferably reacted with one another in a quantitative ratio (B1):(B2) = 10 . 1 to 1:10, preferably 8:1 to 1:8, with particular preference 5:1 to 1:5, and in particular 2.5:1 to 1:2.5.

20 The free-radical graft copolymerization has no special features in terms of method but instead takes place in accordance with the customary and known methods such as are described in the patents EP-A-0 521 928, EP-A-0 522 420, EP-A-0 522 419 or EP-A-0 730 613. It is

25 preferably carried out in the customary and known stirred tanks, stirred tank cascades, tube reactors, loop reactors or Taylor reactors, such as are described, for example, in the patents DE-B-1 071 241 or EP-A-0 498 583 or in the article by K. Kataoka in

Chemical Engineering Science, volume 50, number 9, 1995, pages 1409 to 1416. The Taylor reactors here are designed so that the conditions of Taylor flow are met over the entire length of the reactor, even if the
5 kinematic viscosity of the reaction medium undergoes, as a result of the graft copolymerization, a great change - in particular, increase.

The further essential ingredient of the coating
10 material of the invention is at least one amino resin (C). The amino resin (C) is water-soluble or -dispersible per se or in the presence of the ingredients (A) and (B).

15 Examples of suitable amino resins (C) are melamine resins, guanamine resins, glycoluril resins or urea resins. For further details, refer to Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, 1998, page 29, "amino resins", and the text book "Lackadditive"
20 [Additives for coatings] by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998, pages 242 ff., or to the book "Paints, Coatings and Solvents", second completely revised edition, edit. D. Stoye and W. Freitag, Wiley-VCH, Weinheim, New York, 1998, pages 80 ff. Also
25 suitable are the customary and known amino resins some of whose methylol and/or methoxymethyl groups have been defunctionalized by means of carbamate or allophanate groups. Crosslinking agents of this kind are described in the patents US-A-4 710 542 and EP-B-0 245 700 and

also in the article by B. Singh and coworkers
"Carbamylmethylated Melamines, Novel Crosslinkers for
the Coatings Industry" in Advanced Organic Coatings
Science and Technology Series, 1991, volume 13, pages
5 193 to 207.

Particular preference is given to using low molecular
mass melamine resins (C) which are esterified with
methanol, ethanol, propanol and/or butanol, but
10 especially methanol, and contain on average from 0.05
to 3, preferably from 0.07 to 2.5, and in particular
from 0.08 to 2, imino groups per molecule.

Yet another essential ingredient of the coating
15 material of the invention is at least one color and/or
effect pigment and/or a filler (D).

As effect pigments (D) it is possible to use metal
flake pigments such as commercial aluminum bronzes,
20 aluminum bronzes chromated in accordance with
DE-A-36 36 183, and commercial stainless steel bronzes,
and also nonmetallic effect pigments, such as
pearlescent pigments and interference pigments, for
example. For further details, refer to Römpp Lexikon
25 Lacke und Druckfarben, Georg Thieme Verlag, 1998, pages
176, "effect pigments" and pages 380 and 381 "metal
oxide-mica pigments" to "metal pigments".

Examples of suitable inorganic color pigments (D) are

titanium dioxide, iron oxides, Sicotrans yellow, and carbon black. Examples of suitable organic color pigments (D) are thioindigo pigments Indanthrene blue, Cromophthal red, Irgazine orange, and Heliogen green.

5 For further details, refer to Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, 1998, pages 180 and 181, "iron blue pigments" to "black iron oxide", pages 451 to 453 "pigments" to "pigment volume concentration", page 563 "thioindigo pigments", and
10 page 567 "titanium dioxide pigments".

Examples of suitable fillers (D) are organic and inorganic fillers (D) such as chalk, calcium sulfate, barium sulfate, silicates such as talc or kaolin,
15 silicas, oxides such as aluminum hydroxide or organic fillers such as textile fibers, cellulose fibers, polyethylene fibers or wood flour. For further details, refer to Römpp Lexikon Lacke und Druckfarben, Georg Thieme Verlag, 1998, pages 250 ff., "fillers".

20

The pigments and/or fillers (D) may be incorporated into the coating materials of the invention directly or by way of pigment pastes, in which case suitable grinding resins include in particular the above-
25 described ingredients (A) and/or (B).

The composition of the coating material of the invention may vary very widely and may therefore be adapted to all end uses for which the coating material

of the invention comes into consideration, which is a further particular advantage of the coating material of the invention.

5 Further particular advantages result if the ingredients (A), (B), (C), and (D) are employed in the coating material of the invention in amounts of

10 A) from 2 to 90, preferably from 3 to 80, and in particular from 5 to 70% by weight,

B) from 1 to 80, preferably from 3 to 70, and in particular from 4 to 60% by weight,

15 C) from 1 to 80, preferably from 2 to 70, and in particular from 3 to 60% by weight, and

D) from 1 to 95, preferably from 2 to 90, and in particular from 3 to 85% by weight,

20

the percentages by weight being based in each case on the overall solids content of the coating material, and the amounts of the ingredients (A), (B), (C), and (D) always adding up to 100% by weight.

25

In this context it is further of advantage if the ingredients (A), (B), and (C) are employed in a ratio, based on the solids (nonvolatile fraction) of these ingredients (100%), of (A):(B):(C) = 25-70:10-40:10-40,

preferably 30-50:20-37:20-37, and in particular 40-50:20-35:20-30. In that case the pigments and/or fillers (D) are preferably present in the coating material of the invention in a pigment volume
5 concentration which is sufficient for the hiding ability of a 45 μm thick coating in a single application.

The coating material of the invention may further
10 comprise at least one polyisocyanate (E). Where the coating material of the invention is used in the form of a two-component or multicomponent system in particular as an original refinish material of the invention, the polyisocyanate (E) is an obligatory
15 ingredient.

Suitable polyisocyanates (E) include in principle all of the customary and known aliphatic, cycloaliphatic, aliphatic-cycloaliphatic, aromatic, aliphatic-aromatic
20 and/or cycloaliphatic-aromatic polyisocyanates and polyisocyanate adducts (E) which are used in the paints field and which are also referred to as paint polyisocyanates. Advantageously, these polyisocyanates (E) have on average a functionality of from 2 to 5,
25 preferably from 2.5 to 4.5, and in particular from 2.8 to 4.2, and viscosities of from 100 to 10 000, preferably from 100 to 5 000, mPas. Additionally, the polyisocyanates (E) may have been hydrophilically or hydrophobically modified in a customary and known way.

Examples of suitable polyisocyanate adducts (E) are polyurethane prepolymers containing isocyanate groups, which can be prepared by reacting polyols with an
5 excess of polyisocyanates (E) and/or (b1) and are preferably of low viscosity. It is also possible to use polyisocyanates containing isocyanurate, biuret, allophanate, iminooxadiazinedione, urethane, urea, carbodiimide and/or uretdione groups. Polyisocyanates
10 (E) containing urethane groups, for example, are obtained by reacting some of the isocyanate groups with polyols, such as trimethylolpropane and glycerol, for example.

15 Very particular preference is given to using mixtures of polyisocyanate adducts (E) which contain uretdione and/or isocyanurate groups and/or allophanate groups and are based on hexamethylene diisocyanate, such as are formed by catalytic oligomerization of
20 hexamethylene diisocyanate using appropriate catalysts.

The amount of polyisocyanates (E) in the coating material of the invention may likewise vary very widely. Accordingly, the coating material of the
25 invention in the form of a two-component or multi-component system may very readily be adapted to a very wide variety of requirements which are commonly imposed on such systems, which is yet another particular advantage of the coating material of the invention.

Further particular advantage result if the polyisocyanates (E) are present in the coating material of the invention in an amount of from 0.5 to 50%, preferably from 1 to 40%, and in particular from 2 to 5 30%, by weight based in each case on the overall solids content of the coating material of the invention.

Furthermore, the coating material of the invention may additionally comprise ingredients such as are customary and known in the technological field in question, in 10 customary and known, effective amounts. What is important here is that the further ingredients do not adversely affect, but instead advantageously vary, the advantageous profile of properties of the coating 15 material of the invention.

Examples of suitable further ingredients are cross-linking agents (F), especially compounds or resins containing epoxide groups, tris(alkoxycarbonyl- 20 amino)triazines, compounds or resins containing carbonate groups, blocked polyisocyanates, beta-hydroxyalkylamides, and compounds containing on average at least two groups capable of transesterification, examples being reaction products of malonic diesters 25 and polyisocyanates or of esters and partial esters of polyhydric alcohols of malonic acid with monoisocyanates, such as are described by the European patent EP-A-0 596 460.

If the coating material of the invention is to be curable not only thermally but also with actinic radiation, especially UV radiation and/or electron beams (dual cure), it includes as a further ingredient at least one ingredient (G) which is curable with actinic radiation. Suitable ingredients (G) include in principle all oligomeric and polymeric compounds which are curable with actinic radiation, especially UV radiation and/or electron beams, such as are commonly used in the field of UV-curable or electron-beam-curable coating materials. Advantageously, use is made of radiation-curable binders as ingredients (G). Examples of suitable radiation-curable binders (G) are (meth)acryloyl-functional (meth)acrylic copolymers, polyether acrylates, polyester acrylates, unsaturated polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, silicone acrylates, isocyanato acrylates, and the corresponding methacrylates. In this case the coating material of the invention further advantageously comprises, as a further ingredient, at least one photoinitiator (H), of the Norrish II type, for example, whose mechanism of action is based on an intramolecular variant of the hydrogen abstraction reactions such as occur diversely with photochemical reactions (by way of example, reference may be made here to Römpp Chemie Lexikon, 9th expanded and revised edition, Georg Thieme Verlag Stuttgart, vol. 4, 1991), or cationic photoinitiators (by way of example, reference may be made here to Römpp

Lexikon "Lacke und Druckfarben" Georg Thieme Verlag
Stuttgart, 1998, pages 444 to 446), but especially
benzophenones, benzoin ethers or phosphine
oxides.

5

Further examples of suitable additional ingredients are
reactive diluents (J) for thermal crosslinking and
also, where appropriate, for the crosslinking with
actinic radiation such as branched, cyclic and/or
10 acyclic C₉-C₁₆ alkanes which are functionalized with at
least two hydroxyl groups, preferably dialkyloctane-
diols, especially the positionally isomeric
diethyloctanediols; oligomeric polyols, which are
obtained from oligomeric intermediates which are
15 obtained by metathesis reactions of acyclic monoolefins
and cyclic monoolefins, by the hydroformylation of said
intermediates and their subsequent hydrogenation;
hyperbranched compounds containing a tetrafunctional
central group, such as are described in the patents
20 WO 93/17060 or WO 96/12754 or in the book by
G.R. Newkome, C.N. Moorefield, and F. Vögtle,
"Dendritic Molecules, Concepts, Syntheses,
Perspectives", VCH, Weinheim, New York, 1996;
polycarbonatediols; polyester polyols;
25 poly(meth)acrylatediols; or isocyanate-reactive
solvents such as butyl glycol, 2-methoxypropanol,
n-butanol, methoxybutanol, n-propanol, ethylene glycol
monomethyl ether, ethylene glycol monoethyl ether,
ethylene glycol monobutyl ether, diethylene glycol

monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, trimethylolpropane, ethyl 2-hydroxypropionate or 3-methyl-3-methoxybutanol, and also
5 derivatives based on propylene glycol, e.g., isopropoxypropanol; polysiloxane macromonomers, (meth)acrylic acid and the monofunctional, difunctional and higher polyfunctional esters thereof; maleic acid and its esters and monoesters; monofunctional,
10 difunctional and higher polyfunctional vinyl esters; monofunctional, difunctional and higher polyfunctional vinyl ethers; and also monofunctional, difunctional and higher polyfunctional vinylureas.

15 Further examples of suitable additional ingredients are thermal crosslinking initiators (K) which at from 80 to 120°C form radicals, such as organic peroxides, organic azo compounds or C-C-cleaving initiators such as dialkyl peroxides, peroxocarboxylic acids,
20 peroxodicarbonates, peroxide esters, hydroperoxides, ketone peroxides, azo dinitriles or benzpinacol silyl ethers. C-C-cleaving initiators are particularly preferred since their thermal fission does not give rise to the formation of any gaseous decomposition
25 products which might lead to defects in the paint film.

Further examples of suitable additional ingredients are coatings additives (L) which are preferably not volatile under the processing and application

conditions of the coating material of the invention.
Examples of suitable coatings additives (L) are

- UV absorbers;
- 5 - free-radical scavengers;
- isocyanate crosslinking catalysts such as dibutyltin dilaurate or lithium decanoate;
- slip additives;
- polymerization inhibitors;
- 10 - defoamers;
- antiskinning agents;
- emulsifiers, especially nonionic emulsifiers such as alkoxyated alkanols and polyols, phenols and alkylphenols or anionic emulsifiers such as
- 15 alkali metal salts or ammonium salts of alkanecarboxylic acids, alkanesulfonic acids, and sulfo acids of alkoxyated alkanols and polyols, phenols and alkylphenols;
- wetting agents such as siloxanes, fluorine
- 20 compounds, carboxylic monoesters, phosphoric esters, polyacrylic acids and their copolymers, or polyurethanes;

- adhesion promoters;
 - leveling agents;
 - film formation auxiliaries such as cellulose derivatives;
 - 5 - rheology control additives such as those known from the patents WO 94/22968, EP-A-0 276 501, EP-A-0 249 201 or WO 97/12945; crosslinked polymeric microparticles, such as are disclosed, for example, in EP-A-0 008 127; inorganic
10 phyllosilicates such as aluminum-magnesium silicates, sodium-magnesium phyllosilicates and sodium-magnesium-fluorine-lithium phyllosilicates of the montmorillonite type; silicas such as Aerosils; or synthetic polymers containing ionic
15 and/or associative groups such as polyvinyl alcohol, poly(meth)acrylamide, poly(meth)acrylic acid, polyvinylpyrrolidone, styrene-maleic anhydride copolymers or ethylene-maleic anhydride copolymers and their derivatives, or
20 hydrophobically modified ethoxylated urethanes or polyacrylates;
 - flame retardants and/or
 - biocides.
- 25 Further examples of suitable coatings additives (L) are-

described in the text book "Lackadditive" by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998.

Not least, the coating material of the invention may as
5 a further ingredient include at least one optionally
water-miscible organic solvent (M) such as, for
example, aliphatic, aromatic and/or cycloaliphatic
hydrocarbons such as toluene or methylcyclohexane or
decalin, alkyl esters and alkoxy alkyl esters of acetic
10 acid or propionic acid such as 2-methoxypropyl
1-acetate, alkanols such as ethanol, ketones such as
methyl isobutyl ketone, glycol ethers glycol ether
esters, amides such as N-methylpyrrolidone and/or
ethers such as tetrahydrofuran.

15

The preparation of the coating material of the
invention from its ingredients (A), (B), (C), and (D)
and also, if desired, at least one further ingredient
(F), (G), (H), (J), (L) and/or (M) by the first process
20 of the invention or (A), (B), (C), (D), and also at
least one of said further ingredients on the one hand,
and also (E) on the other hand by the second process of
the invention, has no special features in terms of its
method but instead takes place in a customary and known
25 way by mixing of the ingredients in suitable mixing
equipment such as stirred tanks, dissolvers, extruders
or mixing nozzles in accordance with the processes
which are suitable for preparing the respective coating
materials of the invention.

The coating material of the invention serves for the production of the solid-color topcoat of the invention, including the original refinish of the invention, or of
5 the basecoat of the invention as part of the multicoat color and/or effect paint system of the invention, especially two-coat finish, on primed or unprimed substrates.

10 Suitable coating substrates are in principle all surfaces which are not damaged by curing of the coatings present thereon using heat and, if appropriate, actinic radiation; examples are metals, plastics, wood, ceramic, stone, textile, fiber
15 composites, leather, glass, glass fibers, glass wool, rock wool, mineral-bound and resin-bound building materials, such as plasterboard and cement slabs or roof tiles, and also composites of these materials.

20 Accordingly, the coating material of the invention is in principle also suitable for applications outside of automotive finishing; for example, in industrial coating, including coil coating and container coating. In the context of industrial coatings it is suitable
25 for coating virtually all parts and articles for private or industrial use such as radiators, domestic appliances, small metal parts, hub caps or wheel rims. Furthermore, the coating material of the invention is also suitable for varnishing furniture.

In the case of electrically conductive substrates it is possible to use primers which are produced in a customary and known manner from electrocoat materials.

5 For this purpose, both anodic and cathodic electrocoat materials are suitable, but especially cathodics.

Using the coating material of the invention it is also possible in particular to coat primed or unprimed

10 plastics such as, for example, ABS, AMMA, ASA, CA, CAB, EP, UF, CF, MF, MPF, PF, PAN, PA, PE, HDPE, LDPE, LLDPE, UHMWPE, PET, PMMA, PP, PS, SB, PUR, PVC, RF, SAN, PBT, PPE, POM, PUR-RIM, SMC, BMC, PP-EPDM, and UP (abbreviated codes in accordance with DIN 7728T1). The

15 plastics to be coated may of course also be polymer blends, modified plastics, or fiber reinforced plastics. It is also possible to employ the plastics commonly used in vehicle construction, especially motor vehicle construction. Unfunctionalized and/or nonpolar

20 substrate surfaces may be subjected prior to coating in a known manner to a pretreatment, such as with a plasma or by flaming, or may be provided with a water-based primer.

25 The application of the coating material of the invention has no special features in terms of its method but instead may take place by any customary application method, such as spraying, knife coating, brushing, flow coating, dipping, or rolling. It is

preferred to employ spray application methods, such as compressed air spraying, airless spraying, high-speed rotation, electrostatic spray application (ESTA), for example, alone or in conjunction with hot spray
5 application such as hot air spraying, for example. Application may take place at temperatures of max. 70 to 80°C, so that appropriate application viscosities are attained without any change or damage to the coating material and its overspray (which may be
10 intended for reprocessing) during the short period of thermal stress. For instance, hot spraying may be configured in such a way that the coating material of the invention is heated only very briefly in the spray nozzle or shortly before the spray nozzle.

15

The spray booth used for application may, for example, be operated with a circulation system, which may be temperature-controllable, and which is operated with an appropriate absorption medium for the overspray, an
20 example of such medium being the coating material itself.

Where the coating material of the invention includes further ingredients (G) crosslinkable with actinic
25 radiation, application is made under illumination with visible light with a wavelength of above 550 nm, or in the absence of light. By this means, material alteration or damage to the coating material and to the overspray is avoided.

In the context of the production of the multicoat paint systems of the invention, the application methods described above may be used to produce all coats of the
5 paint system.

In accordance with the invention, the solid-color topcoat or aqueous basecoat film of the invention may be cured thermally and/or with actinic radiation in
10 dependence on its material composition.

Curing may take place after a certain rest period. This period may have a duration of from 30 s to 2 h, preferably from 1 min to 1 h, and in particular from
15 3 min to 30 min. The rest period is used, for example, for leveling and degassing of the coating films or for the evaporation of volatile constituents such as solvents or water. The rest period may be shortened and/or assisted by the application of elevated
20 temperatures up to 80°C, provided this does not entail any damage or alteration to the coating films, such as premature complete crosslinking, for instance.

The thermal curing has no special features in terms of
25 its method but instead takes place in accordance with the customary and known methods such as heating in a forced-air oven or irradiation with IR lamps. Thermal curing may also take place in stages. Advantageously, thermal curing in the case of the original refinish of

the invention is effected at a temperature of from 50 to 100°C, with particular preference from 80 to 100°C, and in particular from 90 to 100°C, for a period of from 1 min up to 2 h, with particular preference from 2 min up to 1 h, and in particular from 3 min to 30 min. Where the substrates used have a high capacity to withstand thermal stress, thermal crosslinking may also be conducted at temperatures above 100°C. In general it is advisable in this case to employ temperatures of 120 to 160°C, preferably 125 to 145°C, and in particular 130 to 145°C (substrate temperature) for a period of 1 min up to 2 h, with particular preference 2 min up to 1 h, and in particular 3 min to 30 min.

Given an appropriate material composition of the coating material of the invention, the thermal curing may be supplemented by curing with actinic radiation, it being possible to use UV radiation and/or electron beams. If desired, it may be supplemented by or conducted with actinic radiation from other radiation sources. In the case of electron beams, it is preferred to operate under an inert gas atmosphere. This may be ensured, for example, by supplying carbon dioxide and/or nitrogen directly to the surface of the coating film.

In the case of curing with UV radiation, as well, it is possible to operate under inert gas in order to prevent

the reaction being inhibited and the formation of ozone.

Curing with actinic radiation is carried out using the
5 customary and known radiation sources and optical
auxiliary measures. Examples of suitable radiation
sources are high or low pressure mercury vapor lamps,
with or without lead doping in order to open up a
radiation window of up to 405 nm, or electron beam
10 sources. The arrangement of these sources is known in
principle and may be adapted to the circumstances of
the workpiece and the process parameters. In the case
of workpieces of complex shape such as automobile
bodies, the regions not accessible to direct radiation
15 (shadow regions) such as cavities, folds and other
structural undercuts may be cured using point, small-
area or all-round emitters, in conjunction with an
automatic movement means for the irradiation of
cavities or edges.

20

The equipment and conditions for these curing methods
are described, for example, in R. Holmes, U.V. and E.B.
Curing Formulations for Printing Inks, Coatings and
Paints, SITA Technology, Academic Press, London, United
25 Kingdom, 1984.

Curing may take place in stages, i.e., by multiple
exposure to light or actinic radiation. This may also
be done alternately, i.e., by curing in alternation

with UV radiation and electron beams.

Where thermal curing and curing with actinic radiation are employed together (dual cure), these methods may be used simultaneously or in alternation. Where the two curing methods are used in alternation, it is possible, for example, to begin with thermal curing and end with actinic radiation curing. In other cases it may prove advantageous to begin and to end with actinic radiation curing. The skilled worker is able to determine the curing method particularly appropriate to each individual case on the basis of his or her general knowledge in the art, possibly with the aid of simple preliminary experiments.

15

The combination of thermal curing and curing with actinic radiation (dual cure) also offers advantages for those coating materials of the invention with a very high pigment content, said advantages consisting in particular in the fact that the solid-color topcoat and original refinish films or the basecoat films are cured mainly by thermal means in their regions close to the substrate and additionally by radiation in their surface regions, leading to coatings which have a particularly high surface quality.

25

In the context of producing the multicoat paint systems of the invention, these curing methods may be employed for producing all coats of the system.

For its use as a solid-color topcoat material of the invention, the coating material of the invention is advantageously applied to substrates which carry
5 surfacer coats or antistonechip primer coats, and cured.

Examples of suitable coating materials which serve for producing surfacer coats comprise as binders, for
10 example, water-soluble or water-dispersible polyesters and/or polyurethanes. Aqueous coating materials of this kind are known from the patents DE-A-43 37 961, DE-A-44 38 504, DE-C-41 42 816 or EP-A-0427 028.

15 When used as an aqueous basecoat material of the invention, the coating material of the invention is preferably applied to the above-described surfacer coats or antistonechip primer coats, predried, and overcoated with at least one clearcoat material, after
20 which the aqueous basecoat film and the clearcoat film or clearcoat films are jointly cured (wet-on-wet technique) to give the multicoat, especially two-coat, color and/or effect paint system of the invention.

25 Suitable clearcoat materials for producing the clearcoat are all customary and known one-component, two-component or multicomponent clearcoat materials, powder clearcoat materials, powder slurry clearcoat materials, or UV-curable clearcoat materials.

Examples of suitable known one-component, two-component or multicomponent clearcoat materials are known from the patents DE-A-42 04 518, US-A-5,474,811, 5 US-A-5,356,669, US-A-5,605,965, WO 94/10211, WO 94/10212, WO 94/10213, EP-A-0 594 068, EP-A-0 594 071, EP-A-0 594 142, EP-A-0 604 992, WO 94/22969, EP-A-0 596 460 or WO 92/22615.

10 One-component (1K) clearcoat materials are known to comprise hydroxyl-containing binders and crosslinking agents such as blocked polyisocyanates, tris(alkoxy-carbonylamino)triazines and/or amino resins. In a further variant, they comprise polymer binders having 15 pendant carbamate and/or allophanate groups, with carbamate- and/or allophanate-modified amino resins as crosslinking agents (cf. US-A-5,474,811, US-A-5,356,669, US-A-5,605,965, WO 94/10211, WO 94/10212, WO 94/10213, EP-A-0 594 068, 20 EP-A-0 594 071 or EP-A-0 594 142).

Familiar essential constituents of two-component (2K) or multicomponent (3K, 4K) clearcoat materials are hydroxyl-containing binders and polyisocyanate 25 crosslinking agents, which are stored separately prior to their use.

Examples of suitable powder clearcoat materials are known, for example, from the German patent

DE-A-42 22 194 or the product information from BASF Lacke + Farben AG entitled "Pulverlacke" [Powder Coating Materials], 1990.

- 5 Essential constituents of powder clearcoat materials include preferably binders containing epoxide groups, and polycarboxylic acid crosslinking agents.

Examples of suitable powder slurry clearcoat materials
10 are known, for example, from the US patent US-A-4,268,542 and from the German patent applications DE-A-195 18 392.4 and DE-A-196 13 547, or are described in the German patent application DE-A-198 14 471.7, unpublished at the priority date of the present
15 specification.

Powder slurry clearcoat materials comprise, as is known, powder clearcoat materials dispersed in an aqueous medium.

20

UV-curable clearcoat materials are disclosed, for example, by the patents EP-A-0 540 884, EP-A-0 568 967 or US-A-4,675,234.

- 25 Of these, the two-component clearcoat materials are used with particular preference.

Depending on color, the solid-color topcoats of the invention have thicknesses of from 15 to 60, preferably

from 18 to 55, with particular preference from 20 to 50, and with in particular from 25 to 45, μm .

The basecoats of the invention have a thickness of from 5 to 50, preferably from 10 to 40, with particular preference from 12 to 30, and in particular from 15 to 25, μm .

The coating material of the invention, especially the solid-color topcoat material of the invention, is outstandingly suitable for the low-emission coating of relatively large objects such as commercial vehicle bodies, where two-coat finishing by the wet-on-wet technique causes great problems. It provides solid-color topcoats which feature good leveling, gloss, topcoat appearance, hardness, and practical solvent and chemical resistance. The coating material of the invention, especially the solid-color topcoat material of the invention, forms an outstanding physical base for the original refinish material of the invention. Said material is outstandingly suitable for the refinishing of commercial vehicles on the line, where it is particularly easy to match the color to the color of the OEM finish. The refinish of the invention adheres extremely well to the OEM finish, and has the same advantageous properties as the latter. It proves to be a particular advantages that the coating material of the invention may also be used as an aqueous basecoat material. In this function, it provides

aqueous basecoat films which, after initial drying, may be overcoated very well with high-solids two-component clearcoat materials, after which the aqueous basecoat film and the clearcoat film may be baked together. The
5 resulting two-coat finish exhibits outstanding inter-coat adhesion. In this way it is possible, in a highly targeted way, to equip those areas on commercial vehicle bodies that require particular protection with a two-coat finish. Such areas are located, in
10 particular, on the outside of the commercial vehicle bodies, where they are subject to a high degree to stress due to stonechipping and/or to the brushes of wash installations. The two-coat finish does not exhibit any adhesion problems in the region of
15 transition to the solid-color topcoat, and its color may be matched very easily, where necessary, to the color of the solid-color topcoat. It proves to be a further particular advantage that the two-coat finish may also be used specifically for decorative purposes,
20 by special formulation with effect pigments, for example, while fully retaining its other advantages.

Examples and comparative experiments

25 Preparation example 1

The preparation of the polyurethane acrylate (B)

In a reaction vessel with stirrer, reflux condenser and

two feed vessels, 63.5 parts by weight of isophorone diisocyanate were added to a mixture of 77.6 parts by weight of a polyester polyol having a number-average molecular weight of 630 and based on adipic acid, 1,6-hexanediol and neopentyl glycol, 9.3 parts by weight of neopentyl glycol, 3.0 parts by weight of trimethylolpropane monoallyl ether, 0.1 parts by weight of dibutyltin dilaurate and 110.2 parts by weight of methyl isobutyl ketone. The reaction mixture is subsequently heated to 105°C. At an isocyanate content of 1.8% by weight, 15.1 parts by weight of trimethylolpropane were added to the reaction mixture and reaction was continued until free isocyanate groups were no longer detectable.

15

At a temperature of 105°C, a mixture of 69.6 parts by weight of n-butyl acrylate, 69.6 parts by weight of methyl methacrylate, 16.6 parts by weight of 2-hydroxypropyl methacrylate and 13 parts by weight of acrylic acid was metered in to the resulting polyurethane over the course of three hours. At the same time, 5.1 parts by weight of tert-butyl perethylhexanoate in solution in 42.8 parts by weight of methyl isobutyl ketone were metered in over the course of 3.5 hours. The reaction mixture was heated to 105°C for 2.5 hours and then cooled to 90°C. Thereafter, 10.6 parts by weight of dimethylethanolamine and 483.2 parts by weight of deionized water were added. Removal of the methyl isobutyl ketone in vacuo

gave a stable, 43% dispersion of the polyurethane acrylate (B) having a pH of 7.9.

Preparation example 2

5

The preparation of the polyester (A)

Into a stainless steel reaction vessel with a volume of 4 l, equipped with a regulatable oil circulation heating system, a close-clearance stirrer, a packed column, a water separator, and a reflux condenser with a return to the top of the column, and also with a temperature measurement means for the reaction mixture and the top of the column, there were weighed the following starting products: 457 parts by weight of hexahydrophthalic acid, 518 parts by weight of a commercial dimer fatty acid having an average molar mass of 527 and an average functionality of 2.03, 398 parts by weight of trimethylolpropane, 605 parts by weight of neopentyl glycol hydroxypivalate, 339 parts by weight of neopentyl glycol and 30 parts by weight of cyclohexane as azeotrope performer. The starting products were melted and heated to 155°C. The resulting melt was heated to 220°C over six hours with stirring. The raising of the temperature was carried out in such a way that the temperature at the top of the column did not exceed 85°C. The resulting reaction product was held at 220°C until an acid numbers of 10.5 mg KOH/g had been reached. Thereafter it was cooled to 150°C,

after which 398 parts by weight of trimellitic anhydride were added. The resulting reaction mixture was again heated to 175°C and held at this temperature until an acid number of 33.2 and a viscosity of 235 mPas (measured on a 50% strength solution of the reaction mixture in ethylene glycol mono-n-butyl ether in an ICI cone and plate viscometer, cone C, at 23°C) had been reached. Thereafter it was immediately cooled to 130°C and dissolved with 900 parts by weight of ethylene glycol mono-n-butyl ether.

The resulting solution was cooled to below 100°C and admixed with 105 parts by weight of dimethylethanolamine. The neutralized solution was dispersed in 1 000 parts by weight of deionized water and then adjusted with further deionized water to a solids content (one hour; 130°C) of 55% by weight. The resulting aqueous dispersion of the polyester (A) was weakly opaque and had a pH of 7.55. The polyester (A) had an acid number of 33.2 mg KOH/g, a hydroxyl number of 159 mg KOH/g, a number-average molar mass of 1 250, and a degree of branching of 1.78 mol/kg.

Preparation example 3

25

The preparation of a pigment paste comprising white pigments

In a laboratory dissolver, 450 parts by weight of the

dispersion of the polyurethane acrylate (B) from preparation example 1 were weighed in. With stirring (4 m/s), the following were added in this order: 20 parts by weight of isopropoxypropanol, 10 parts by weight of a commercial, nonionic polyurethane containing specific anchor groups, as a pigment dispersing aid, 20 parts by weight of deionized water and 500 parts by weight of a commercial titanium dioxide pigment of the rutile type with appropriate surface treatment. The resulting mixture was then treated in a dissolver at a speed of 20 m/s for five minutes. The mixture was then milled on a customary, continuous stirred laboratory mill containing (with a filling level of 75%) SAZ bead grinding media with a diameter of from 1.0 to 1.6 mm, with a rotor speed of 7.5 m/s. This introduced a specific energy of 75 Wh/kg. The temperature during the grinding operation was held at below 40°C. The result was an aqueous pigment paste having a pigment distribution as required for producing high-gloss solid-color topcoats.

Example 1

The preparation of an inventive white solid-color topcoat material

The following constituents, in the order stated, were weighed out into a stainless steel stirred vessel and homogenized by stirring following each addition:

209 parts by weight of the polyester (A) from preparation example 2, 18 parts by weight of N-methylpyrrolidone, 27 parts by weight of an aliphatic hydrocarbon mixture having a boiling range of from 180 to 210°C, 5 parts by weight of dimethylethanolamine, 92 parts by weight of a low molecular mass melamine resin etherified with methanol and containing imino groups, 5 parts by weight of 2-methyl-1-propanol, 437 parts by weight of the pigment paste as per preparation example 3, 13 parts by weight of a commercial acrylate thickener (25% in deionized water) and 185 parts by weight of deionized water. The result was a white solid-color topcoat material having a nonvolatiles content of 50% by weight and a viscosity of 1 500 mPas at a shear rate of 500 s⁻¹ in a rotational viscometer.

Example 2

The preparation of an inventive original refinish material

To 500 parts by weight of the inventive white topcoat material of example 1 there were added 35 parts by weight of a commercial hexamethylene diisocyanate oligomer with a narrow molar mass distribution (75% in 2-methoxypropyl 1-acetate) and 2.5 parts by weight of a 1% strength solution of dibutyltin dilaurate in 2-methoxypropyl 1-acetate. The resulting mixture was homogenized with a customary laboratory stirrer. The

result was a white original refinish material having a nonvolatiles content of 51% by weight and a stability time or processing time of up to four hours.

5 **Example 3 and 4**

The production of an inventive solid-color topcoat material and of an inventive original refinish coat

10 The solid-color topcoat material of example 1 (example 3) and the original refinish material of example 2 (example 4) were applied to standard metal bodywork panels which had been coated with a 20 μm electrocoat, produced from a commercial cationic
15 electrocoat material, and with a 35 μm surfacer coat, produced from a standard commercial pale gray water-based surfacer. For this purpose, the coating materials were adjusted to an efflux viscosity of 60'' (DIN 20/4) using deionized water.

20

For example 3, the solid-color topcoat material of example 1 was applied using a high-performance pneumatic spray gun so as to give, after baking, a coat thickness of 43 μm . Following application, the solid-
25 color topcoat film was flashed off at room temperature for 10 minutes, predried at 80°C for 10 minutes, and then baked in a forced-air oven at 140°C (substrate temperature) for 20 minutes. The performance properties of the resulting inventive solid-color topcoat can be

found in the table.

For example 4, the original refinish material of example 2 was applied in the same way to the solid-color topcoat of example 3 so as to give, after curing, a coat thickness of 41 μm . Following its application, the refinish film was flashed off at room temperature for 10 minutes and then dried in a forced-air oven at 100°C for 30 minutes. The performance properties of the resulting inventive refinish coat can likewise be found in the table.

Table 1: Performance properties of the solid-color topcoat (example 3) and of the refinish coat (example 4)

Properties	Example 3	Example 4
Gardner gloss at 20° (%)	84	86
Adhesion by the cross-cut test to DIN ISO 2409: 1994-10	GT0	GT0
Hardness by the König pendulum attenuation test (s)	154	140
Solvent resistance in the acetone test (double rubs)	>200	>200

VDA* stonechip resistance,

2x500g, 2 bar (index)	2	2
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Erichsen cupping

(DIN EN ISO 1520:1995-04)	6.6	6.0
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* VDA = German automakers' association

The values in the table underscore the advantageousness
5 of the inventive solid-color topcoat materials and
original refinish materials. Over and above this, a far
smaller amount of volatile organic constituents,
especially organic solvents, were released during the
production of the inventive solid-color topcoats than
10 during the production of a customary and known two-coat
finish for which a solventborne two-component clearcoat
material was used. At the same time, for the finishing
of commercial vehicles, the optical and other
properties of the inventive solid-color topcoat proved
15 an equal match for, if not superior to, those of the
customary and known two-coat finish.